# Synthesis of Biomorphic $Fe_2O_3$ Fibers Derived from Silk Template

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**Abstract.** Natural silk fibers were used as the template to synthesis biomorphic $Fe_2O_3$ fibers. Silk fibers were first immersed into a $Fe(NO_3)_3$ solution and then sintered in air at high temperatures to produce the final $Fe_2O_3$ fibers. Their microstructures, phases, and synthesis process were analyzed. The results show that these synthesized fibers retained the morphologies of silk faithfully. The concentration of the $Fe(NO_3)_3$ solution, the soak period, and the sintering temperatures all had the effect on the continuity of the biomorphic fibers. The fabrication process of biomorphic ceramic included the formation of $Fe_2O_3$ and removal of their silk templates.

## Introduction

Recently, ceramics mimicking the bio-structures of natural tissues have attracted increasing interest. In comparison to synthetic materials, natural materials such as bamboo, wood, cotton, etc., possess intricate and graceful microstructures formed in a long-term evolution process. Researchers have used these bio-structures as templates to fabricate desired ceramics such as SiC, TiC, $Al_2O_3$, $SnO_2$, etc., that retained the micro-morphologies of their original counterparts[1-7]. Results show that natural bio-structures can play an important role in obtaining new ceramic materials with excellent properties. The method of using the bio-templates provided a new and effective way to fabricate the materials with excellent properties.

In industry, ferric oxide ($Fe_2O_3$) is an important product that can be often used for magnetic recording media, catalysts, pigments, water treatment, gas sensors, optical devices, electromagnetic devices, and so on[8-9]. These days, $Fe_2O_3$ can be obtained by many traditional techniques such as the sol-gel method, the combustion method, the thermal decomposition method, the hydrolyze method, the hydrothermal method, the catalysis method, etc[9-10]. Through these traditional methods, the $Fe_2O_3$ particles of many shapes, including spheres, cubes, rods and platelets, can be prepared. However, there are few reports about the $Fe_2O_3$ with fibriform shapes. Silk is an animal fiber made by silkworms. The main component of the silk is protein. In the present work, we select silk as a natural template to prepare a biomorphic $Fe_2O_3$ with the shape of fiber. Their microstructures, phases, and synthesis process were investigated. We hope this method could provide a new way to fabricate $Fe_2O_3$ with its shape controlled by the nature.

## Experimental

### Sample Preparation

The natural silk fibers were selected as the template to prepare $Fe_2O_3$ fibers. Dried and loose silk fibers were first immersed into a $Fe(NO_3)_3$ solution. After drying at 50℃ for 24h, they were then placed in an oxidation furnace and sintered at certain temperature for 2h. The rate of heating is

 

2 ℃/min. Thus, the silk templates were removed and $Fe_2O_3$ fibers were obtained. During the course of manufacture, we used seven pieces of silk and processed them with different concentration of the $Fe(NO_3)_3$ solution, soak period, and sintering temperature to get seven different $Fe_2O_3$ samples. Table 1 lists the processing parameters for these seven samples.

## Characterization

The phases of the materials obtained in this study were identified by an X-ray diffractometer (XRD, Cu-Kα, RigakuX 2038, Japan). The microstructures of the materials were observed by using a scanning electronic microscope (SEM, JSM-6380, JEOL, Japan). The immersed silk and the original silk without immersing in solution were analyzed with a thermogravimetric analyzer (TG-DSC, SDT Q600, TA Instruments, US) in air. The temperature ranged from room temperature to 1000 ℃. The heating rate was 20 ℃/min.

## Results and Discussion

Fig.1 shows the full scale photo of silk and the $Fe_2O_3$ derived from silk. It is obvious that this pile of material is composed of fibers, which indicates that the $Fe_2O_3$ got the fibriform shape of silk.

The XRD patterns of the materials derived from silk at different sintering temperatures were shown in Fig.2. The XRD patterns show that the component of these biomorphic fibers is $Fe_2O_3$.

Fig.3 shows the microstructures of the biomorphic $Fe_2O_3$ processed with different parameters. The serial number of each image is corresponding to that of the sample, as shown in Table 1. It can be seen that these fibers retain the original fibrous silk morphology well, as compared with the microstructure of the silk in Fig.1. The diameters of the $Fe_2O_3$ fibers are in the range of 5-10μm. The conformation of these $Fe_2O_3$ fibers is controlled by nature, which is different from the traditional oxide fibers.

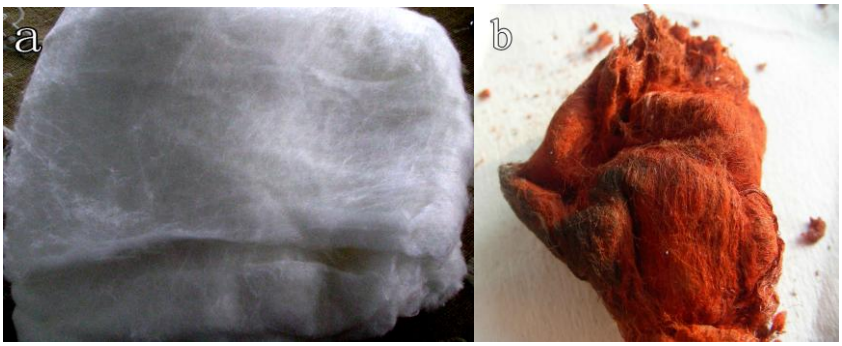


Fig.1 Full Scale Photo of (a) Silk and (b) the Biomorphic $Fe_2O_3$

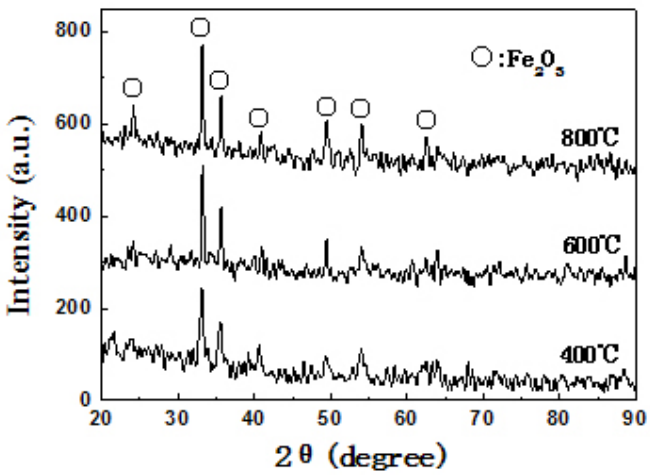


Fig.2 XRD Pattern of $Fe_2O_3$ Derived from Silk at Different Sintering Temperatures

Tab.1 The Processing Parameters for the $Fe_2O_3$ Samples

| Serial number | Concentration of the $Fe(NO_3)_3$ solution (%) | Soak period (min) | Sintering temperature (℃) |
|---|---|---|---|
| a | 10 | 10 | 600 |
| b | 20 | 10 | 600 |
| c | 30 | 10 | 600 |
| d | 20 | 1 | 600 |
| e | 20 | 120 | 600 |
| f | 20 | 10 | 400 |
| g | 20 | 10 | 800 |

Fig.3 a, b, and c show the microstructures of the $Fe_2O_3$ fibers obtained by soaking in different concentration of the solution. It is obvious that the continuity of the fiber after soaking in the solution of higher concentration is better than that of lower concentration. The fibers in Fig. 3a are broken and shorter, but the fibers in Fig. 3b and c are longer. This is because that more $Fe(NO_3)_3$ solute covered the surface of the silk fibers after soaking in the solution of higher concentration. Then, more $Fe_2O_3$ formed and covered the silk after sintering. Thus, this $Fe_2O_3$ fiber was stronger to keep the shape of silk more perfectly when the silk-template was removed. Therefore, their continuity was improved with the increasing of the concentration.

Fig.3 d, b, and e show the microstructures of the $Fe_2O_3$ fibers obtained by soaking in the solution for different period. The other processing parameters were same for each. It can be seen that the continuity of the $Fe_2O_3$ fiber with longer soak period is better than that with shorter soak period. This is because that more $Fe(NO_3)_3$ solute infiltrated in the silk after soaking for longer period, which led to more $Fe_2O_3$ and stronger fibers after sintering.

Fig.3 f, b and g show the microstructures of the $Fe_2O_3$ fibers sintered at different temperatures. The other processing parameters were also same for each. Compared to the $Fe_2O_3$ fibers sintered at 400 ℃ (Fig.3 f), the continuity of the fibers sintered at 600 and 800 ℃ (Fig.3 b and g) exhibits a little better. This is due to their higher degree of crystallization than the fiber sintered at 400 ℃ that is shown in Fig.2, which can lead top stronger and longer fibers.

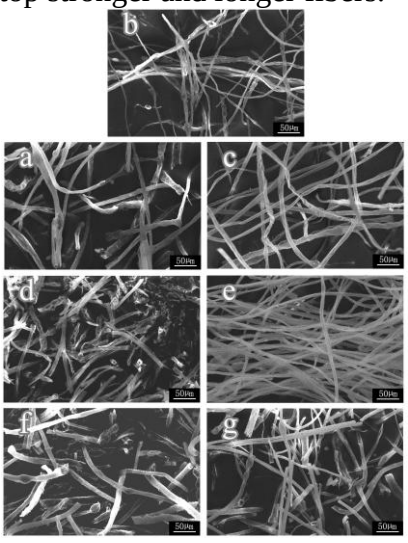


Fig.3 SEM Images of Biomorphic $Fe_2O_3$ Fibers (the Serial Number of Each Image is corresponding to that of the Sample Shown in Tab.1)

Fig.4a shows the TG-DSC thermogram of the original silk without immersing in the solution. There is a remarkable weight lost between 250 ℃ and 670 ℃, with some exothermic peaks being found at 387, 532 and 656 ℃. This is due to the decomposition and burning of the silk.

Fig.4b shows the TG-DSC thermogram of the immersed samples below 1000 ℃. As shown in this figure, there is an obvious endothermic peak at 82℃, corresponding to about 29% weight loss.

It can be attributed to the dehydration of the ferric nitrate nonahydrate. The exothermic peak at 167 ℃ corresponding to 30% weight loss is caused by decomposition of $Fe(NO_3)_3$ to form $Fe_2O_3$. There are another two exothermic peaks found at 318 ℃ and 478 ℃ with 37% weight loss. This may be due to the decomposition and burning of the silk. Since the $Fe_2O_3$ formed before the removal of the silk-template, the fibrous morphology of the silk could be retained to this $Fe_2O_3$.

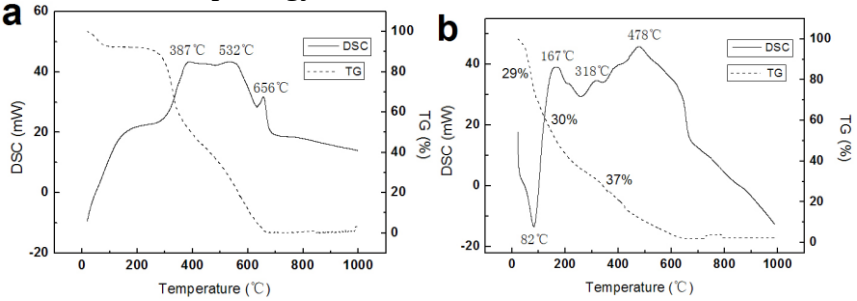


Fig.4 TG-DSC Thermograms of the Original Silk (a) and the Immersed Silk (b)

## Conclusion

This study provided a new method to fabricate biomorphic $Fe_2O_3$ fibers by using natural silk fibers as a bio-template. The processing principle of bio-template technologies was to treat the silk fibers with an inorganic solution and then to sinter at high temperature to form biomorphic ceramics. The $Fe_2O_3$ fibers retained the basic fibrous silk morphology well. The concentration of the solution, the soak period, and the sintering temperatures can influence the continuity of the biomorphic $Fe_2O_3$ fibers. The fabrication process of biomorphic ceramic included the formation of $Fe_2O_3$ and removal of their silk templates. Since it is different from the traditional fibers with their structures obtained artificially, this method of using bio-template could provide a new idea for designing of oxide fiber.

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